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Performance enhancement in latent heat thermal storage system: A review

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ABSTRACT

Phase change material (PCM) based latent heat thermal storage (LHTS) systems offer a challenging option to be employed as an effective energy storage and retrieval device. The performance of LHTS systems is limited by the poor thermal conductivity of PCMs employed. Successful large-scale utilization of LHTS systems thus depends on the extent to which the performance can be improved. A great deal of work both experimental and theoretical on different performance enhancement techniques has been reported in the literature. This paper reviews the implementation of those techniques in different configurations of LHTS systems. The influence of enhancement techniques on the thermal response of the PCM in terms of phase change rate and amount of latent heat stored/retrieved has been addressed as a main aspect. Issues related to mathematical modeling of LHTS systems employing enhancement techniques are also discussed.

Contents

1. Introduction

The increasing gap between the global demand and supply of energy is becoming a major threat as well as a challenge for the engineering community to fulfill the needs of the energy hungry society. Many forums and energy management groups have been formed to emphasize the storage of energy in both industrial and domestic sectors, in any possible form. The utilization of the abundant source—solar thermal energy and hot waste streams available in industries has attracted the scientific community to provide attractive solutions for the problems on energy conservation and storage/retrieval.

Thermal energy can be stored in the form of sensible heat in which the temperature of the storage material varies with the amount of energy stored. Water or rock can be the best example [1]. Alternatively, thermal energy can be stored as latent heat in which energy is stored when a substance changes from one phase to another by either melting or freezing. The temperature of the substance remains constant during phase change.

Of the two, latent heat thermal energy storage technique has proved to be a better engineering option due to its various advantages like large energy storage for a given volume, uniform

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Table 1
Applications of LHTS units.

S. no.	Fields
1	Solar based dynamic space power generation
2	Solar thermal applications
3	Industrial waste heat recovery
4	Automobiles
5	Cooling of electronics
6	Textiles
7	Passive heating of buildings
8	Air conditioning systems

energy storage/supply, compactness, etc. Hence, different configurations of latent heat thermal storage (LHTS) units find their wide applications in various engineering fields which are listed in Table 1.

A summary of various practical applications of LHTS units can be found in Refs. [2,3]. LHTS units employ phase change materials (PCMs) which undergo change of phase (solid-to-liquid and vice versa) during the energy transfer process. During the last four decades many such materials, with wide range of melting/freezing point, have been identified and studied extensively. These materials include organic (e.g. paraffin), inorganic (e.g. salt hydrates) and salt eutectics (e.g. $CaCl_2{\cdot}MgCl_2{\cdot}H_2o$). Wide range of PCMs with their properties, advantages and limitations have been comprehensively reported in Refs. [2–4].

Though LHTS units serve as a better energy storage device as they have a high thermal energy density and possess a nearly isothermal operation, the phase change material loaded in the unit possesses a very low thermal conductivity, which drastically affects the performance of the unit. The effect of the lower value of conductivity is reflected during energy retrieval or withdrawal with an appreciable temperature drop during the process. As a result, the rate of phase change process (melting/solidification of PCM) has not been up to the expected level and the large-scale utilization of LHTS units, remains unsuccessful. Therefore, to tackle the above-mentioned drawbacks, it becomes necessary to improve the thermal performance of the LHTS units employing PCMs. The various techniques adopted for enhancing the thermal performance of the LHTS units are enumerated below:

- Using extended surfaces.
- Employing multiple PCM's method.
- Thermal conductivity enhancement.
- Micro-encapsulation of PCM.

This paper presents a review on these performance enhancement techniques in order to provide information on relative merits and demerits of the various possible enhancement techniques.

2. Using extended surfaces

Fins or extended surfaces are used to provide additional heat transfer surface in thermal systems. In LHTS, the role of different configurations of fins in enhancing the performance has been studied extensively by various researchers. The LHTS, studied until now, are of two types:

System packed with PCM which transfers heat with a hot/cold heat transfer fluid (HTF), the one used in solar water heaters, space based power plants, waste heat recovery systems, etc.
System packed with PCM transfers heat with hot/cold boundary wall, the one used in electronic cooling.

The location of the fins in systems where there is no HTF is obviously at the PCM side. But if the PCM transfers the heat with HTF, the location of the fins is generally based on the relative heat transfer coefficient. This is because, the efficiency of fin increases with decrease in heat transfer coefficient [5]. In most of the systems, the PCM side heat transfer coefficient is less than that of the HTF side and thus it is a general practice that fins are on PCM side. However, it is important to understand that whether the presence of fins does really give the appreciable performance enhancement or not. Because the governing heat transfer mechanisms may be different for different phase change processes (melting and solidification). Moreover, the heat transfer mechanisms during the phase change processes depend upon the configuration and orientation of the system and fins. The proceeding discussions deal with heat transfer mechanisms and role of fins in determining the modes of heat transfer during melting and solidification separately.

2.1. Melting

During melting, heat is transferred to the PCM first by conduction and later by natural convection. This is because, the solid region moves away from the heat transfer surface and the thickness of the liquid region increases near the heat transfer surface. Since thermal conductivity of liquid PCM is less than that of solid PCM, the heat transfer by conduction almost becomes negligible as the melting process continues. The further melting is mostly by natural convection due to the density gradient that exists within the liquid PCM.

The influence of natural convection on the location of melt front has been investigated by Lamberg and Siren [6]. The melting in a semi-infinite PCM storage, with an internal fin, was studied analytically. The analytical model consists of the well-known Newmann solution, which assumes that the heat is transferred only by conduction and natural convection can be negligible. It is found that though Newmann solution is exact solution, it underestimates the location of the melt front.

Lamberg et al. [7] conducted numerical study on melting of PCM in a rectangular enclosure with and without the natural convection effect and the results were compared with experimental results. It was observed from the results that when the natural convection effect was ignored, the PCM took double the time of actually it takes in reality to reach the maximum temperature.

Stritih [8] traced the interface location during melting of PCM in a rectangular storage through experimental work. The experimental results were compared with conduction based analytical solution. Only at the beginning of melting process, the analytical results showed good agreement with experimental results. Once melting began, the experimental interface location was much ahead of that one obtained from analytical calculation.

Zhang et al. [9] experimentally studied the melting of n-octadecane, which was discretely heated at a constant rate from one side of an enclosure. During the melting process as time passed, the temperature in the upper region of the liquid was found to be higher than that in the lower region, consequently accelerating the melting process. It was due to the reason that natural convection of the liquid phase was developed, which led to the ascending of hot liquid and the descending of cold liquid. The discrete heat sources had nearly the same temperatures only at the early stage of the process. This indicates that the early stage of heat transfer is conduction controlled. As the melting process progressed, the surface temperatures became different, increasing from top to bottom, which means the further heat transfer was convection dominated.

Jellouli et al. [10] dealt with the melting of PCM in rectangular enclosure heated from below. The isotherms obtained from the numerical study revealed the conduction dominated melting

process at the early stage, as they were parallel to the hot bottom side of the enclosure. As time elapsed, the deformation of the isotherms from the horizontal became more accentuated. Since the deformation of the isotherms from the horizontal is a clear indication of effect of convection, it is concluded that the mechanism of heat transfer was gradually shifted to natural convection.

Like in rectangular enclosure, natural convection has also been found as dominant heat transfer mechanism in cylindrical and spherical enclosures. Ng et al. [11] investigated the melting of PCM stored in a horizontal cylindrical annulus heated isothermally from inside. The natural convection was modeled by Boussinesq approximation. The results showed recirculation cells which are representations of natural convection flow in the liquid PCM. Regin et al. [12] analyzed the melting behavior of paraffin wax encapsulated in a cylindrical capsule surrounded by hot water. The experimental results showed the influence of natural convection on the melting process as the process occurred axisymmetrically, i.e. melting in top region was much faster than that in bottom region. It is also reported that better agreement between numerical results and experimental results could be achieved only after including the natural convection in the numerical modeling.

Jones et al. [13] conducted experimental and numerical study on melting of PCM in cylinder heated from side vertical wall. Digital photographs, which were taken during the melting process, revealed that only in earlier stages of melting, the melt layer thickness was uniform along the vertical direction (conduction dominated). As the time elapsed, the melt layer thickness began to vary along the vertical direction. This is the indication of convection dominated melting. The shapes of the melt front at different times are similar to that of observed in rectangular enclosures. Akgun et al. [14] observed similar kind of heat transfer during the experimental work on melting of paraffin in a tube in shell configuration, which was oriented vertically. When the PCM was heated from inner wall, the molten PCM extended radially outward and the molten region established a conical shape. This is because the convection heat transfer drives the recirculation inside the molten PCM.

Though spherical system provides largest volume per unit surface area, only limited study could be found on their application in LHTS systems. However, a detailed experimental study by Bahrami [15] provides the details of phase change process in spheres. Although the solid–liquid interface was flat in the beginning of melting, in very short period it assumed a dome-like shape. The dome-like shape of interface remained unchanged till the end of melting. This is an indication of more melting at the upper portion of the spherical container. More at the upper portion is due to the fact that the solid sinks to the bottom as the solid PCM is heavier than the liquid PCM. Hence, solid PCM is in contact with the lower wall of the sphere through out the melting process. This is termed as unconstrained melting by Tan [16]. It is also reported that the melting at the top portion was still mainly due to natural convection as the natural convection cells were observed during the entire melting process. The experimental study by Tan [16] was also extended to constrained melting in which the solid PCM was held to prevent it from sinking down to the bottom. The asymmetric melting was more pronounced in constrained melting. The digital images revealed that the melting front took oval-shaped pattern during the melting due to the existence of natural convection cells at the top and bottom halves of the sphere. However, faster melting was observed at the top portion as stronger natural convection prevailed at top. Similarly, the melting process in spheres was found to be asymmetric by Ettouney et al. [17]. Due to temperature gradient, hotter melt at the base of the sphere could rise upward and loses part of heat to the cooler melt and solid PCM. As a result, natural convection was initiated and started diminishing the role of conduction.

From these studies, it is clear that during the melting process, the heat transfer is dominated by natural convection. The domination of natural convection during melting of PCM in various geometries of LHTS has been illustrated in Fig. 1. As it can

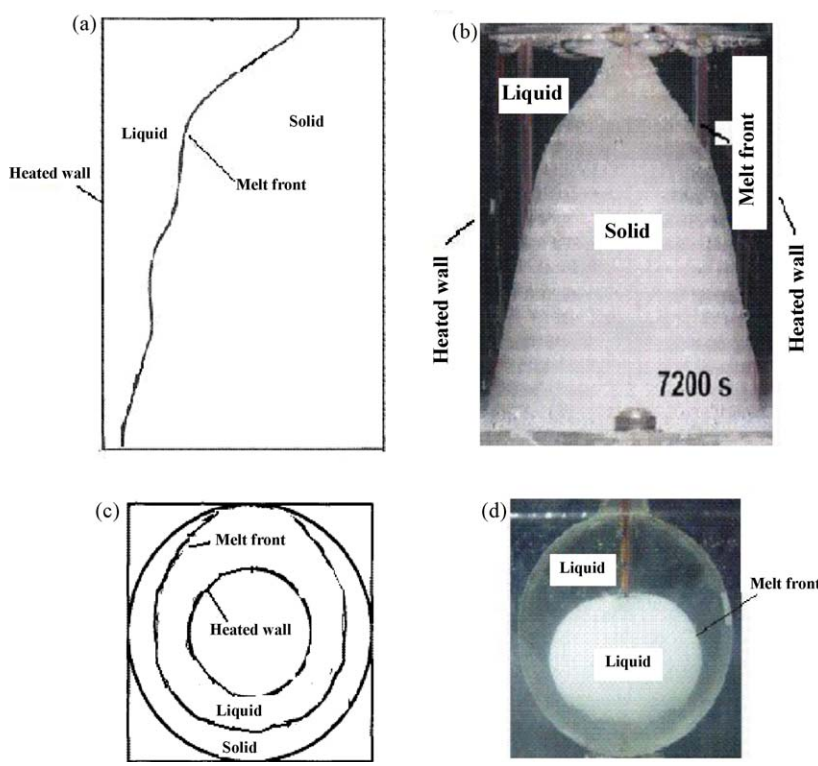


Fig. 1. Natural convection dominated melting process: (a) rectangular system [9]; (b) cylindrical system [13]; (c) cylindrical annulus [11]; (d) spherical system [16].

be seen, due to natural convection more melting takes place in the top portion of all types of geometries. Therefore, if fins are provided on PCM side, then the presence of fins should not necessarily be for improving the conduction rate, but more importantly for improving the natural convection process. However, when top wall of the rectangular system is used as heated wall, then melting would be dominated by conduction for longer period of time. This has been revealed by Lacroix and Benmadda [18] as the isotherms obtained were parallel to the heated top wall. The temperature gradient was found in the negative *y*-direction and thus condition became stable. Even the existence of buoyancy driven flows in the molten PCM could be noticed, they were found to be relatively weak. Because of the absence of natural convection, in the top wall heating system, the melting process took more time (approximately double) as compared to bottom wall heating. Similarly, only conduction dominated melting process was observed by Ettouney et al. [19], when the HTF was allowed to flow downward in a vertical shell and tube configuration. Hence, the role of natural convection in the melting process can be ruled out in a rectangular module with top wall heating. However, if the system with top wall heating is coupled with environment, i.e. the bottom wall is not at adiabatic condition, then natural circulation in the liquid phase could be expected [20]. The melting of PCM in a vertical cylinder (since it was a two-dimensional formulation, the resulting system is nothing but rectangular cavity) from the top was investigated by Pinelli et al. [21]. Although the results of conduction based numerical study could show good agreement with experimental results, considerable difference was observed at advanced stages of melting. In the extended study on the same configuration by Pinelli and Piva [20], natural convection was accounted for. The numerical results showed significant quantitative improvement in the agreement with experimental data. This indicates that natural convection exists even in top wall heating system, as the system is coupled with environment. Reddy [22] conducted numerical study on the melting process in a tilted rectangular cavity, which is a solar integrated collector water heating system. The top wall was used as solar radiation receiver and through the bottom wall the stored heat was supplied from melted PCM to cold water. The simulation was performed without fins and with 4, 9 and 19 fins. The liquid fraction of PCM was observed after 24 h. Although all the finned systems showed good amount of melting as compared to unfinned system, only system with 9 fins was observed with 95% of melting. This means, the system with 9 fins provided optimum performance.

Rectangular module is a basic heat storage unit that is related to various areas such as solar energy system, geothermal energy, nuclear reactors, etc., because of its simplicity [23]. Since it is simple in geometry and boundary conditions, extensive study has been made so far. In the numerical study on top wall heated rectangular module by Akhilesh et al. [24], the natural convection was ignored. As mentioned above, if the system is not coupled with environment, this assumption is reasonable and realistic. The analysis included the effect of adding more number of fins per unit length on the melting process. More number of fins per unit length led to more heat transfer area and thus energy stored. However, it was found that beyond a value (which is termed as critical value by authors) increasing number of fins could not enhance the performance considerably. Gharebaghi and Sezai [25] investigated the performance enhancement in the rectangular device due to horizontal fins added to the vertical heated walls. Both the heated walls were kept at a constant temperature and higher than the melting point of the PCM. The results indicated that the heat transfer rate could be increased due to the presence of fins. It is also reported that vertical heated walls with horizontal fins should be preferred to horizontal heated walls with vertical fins, as the former resulted in double the heat transfer rate as compared to the latter. The heat transfer enhancement factor was found to be increasing as the distance between the adjacent fins was decreased (corresponding to system with more number of fins). From the results, it can be interpreted that beyond some value, increasing the number of fins would lead to only marginal increase in heat transfer rate. This is because, as the number of fins is increased then there will be a hampering effect on the buoyancy driven flows and the melting becomes conduction-dominated process [26].

Lacroix and Benmadda [26] studied the melting process in a rectangular enclosure under the influence of horizontal fins emerging from vertical heated wall (Fig. 2). The numerical simulation included the effect of number of fins and length of fins on the melting rate. In case of shorter fins, the melting rate was almost independent of number fins. It was also found that once the melting front crossed the tip of the fins, the melting process became similar to that of a case without fins. Hence, the presence of fins was hardly felt. On the other hand, more number of longer fins could steadily enhance the melting rate in all cases. At higher values of heated wall temperature, increasing the number of fins produced only little enhancement in melting rate. This is due to the hampering effect on the buoyancy driven flows. This shows that the optimum number of fins depends on temperature of heated wall. It is concluded that few longer fins (4 fins of 0.03 m long each) are far more efficient in enhancing the melting rate than more number of shorter fins (19 fins of 0.01 m long each). Few longer fins could enhance the melting rate significantly even with small temperature difference between heated wall and melting point. This was found to be more efficient as compared to increasing the temperature of heated wall above the melting point. Similar kind of system was also studied by Lamberg et al. [7] and Lamberg [27]. Since the objective of the work was to validate the numerical results, no attempt was made to study the effect of number of horizontal fins on melting process. However, a system with two fins was compared with system with no fin. The experimental results indicated that considerable enhancement in the melting rate is realistic in rectangular enclosure with horizontal fins.

In electronic devices, such as computers, digital cameras, cellular phones, etc., heat sinks have been in use for cooling of the

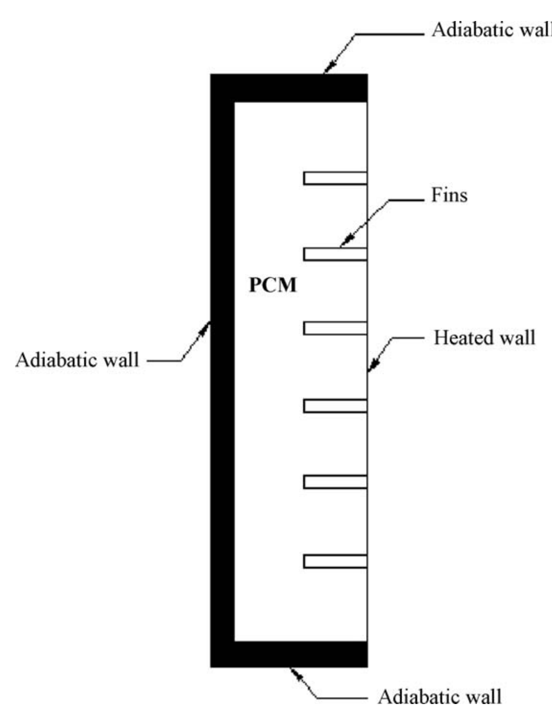


Fig. 2. Rectangular LHTS unit with horizontal fins emerging from vertical heated wall [26].

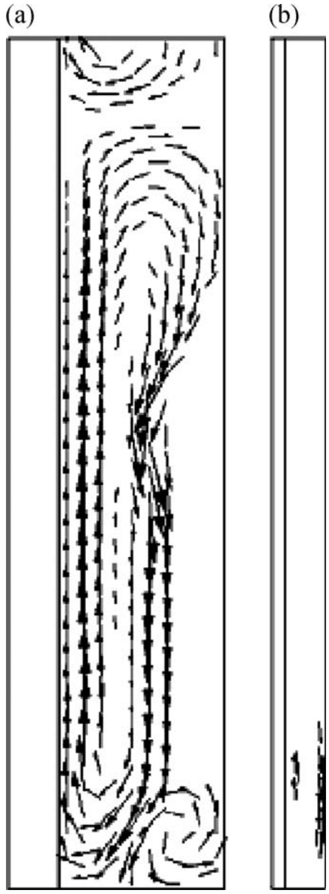


Fig. 3. Fluid motion during melting [28]: (a) wider system; (b) narrow system [30].

components. Such heat sinks are simple rectangular modules with internal fins. In recent years, PCM based heat sinks (PCM is packed between the fins) have been studied widely. Different modules of PCM based heat sinks studied are heat sinks with vertical fins emerging from top heated surface [24], heat sinks with horizontal fins emerging from vertical heated surface in which portion of the fin tips immersed in PCM [26], heat sinks with vertical fins emerging from heated bottom surface [29–31], etc. These studies have mainly focused on performance enhancement as a result of adding PCM in the conventional finned heat sink rather than adding fins in the PCM. However, the effect of vertical fins emerging from heated bottom surface can still be explored from Shatikian et al. [30] and Shatikian et al. [31]. They studied the melting of PCM for different thickness of PCM stored between fins (wider and narrow cases) and different fin thickness. For a fixed size of rectangular module, wider system corresponds to system with less number of fins and vice versa. The results showed that the melting rate in the narrow cases was faster than that of in the wider cases. It was found that in wider cases, the fluid motion became stronger and stronger as the melting progressed. On the other hand, in narrow cases, the fluid motion was hardly seen even at advanced stages of melting. The intensity of the fluid motion in wider and narrow cases has been illustrated in Fig. 3.

Lacroix and Benmadda [18] also noticed that the onset of natural convection was gradually prevented when the distance between the fins was decreased. Therefore, it can be concluded that natural convection would exist if less number of fins are used. However, Lacroix and Benmadda [18] found that too large distance between the fins led to the reduction in total heat transfer surface area. This means for a fixed size of module, it is important to optimize the distance between the fins, i.e. number of fins. As mentioned earlier, Reddy [22] has found that increasing the number of fins from 9 to 19 caused slow melting rate. Although for the system studied, optimum number of fins has been declared, this cannot be generalized as no non-dimensional analysis was carried out. According to Lacroix and Benmadda [18] the optimum distance between the fins decreases as Rayleigh number increases and thus, this has been expressed as a function of Rayleigh number, which is valid for $2 \times 10^6 \geq Ra_H \leq 8.57 \times 10^6$ (Fig. 4). The expression suggested is

$$W = a\,RaH + b$$

where W is distance between the fins, Ra_H is Rayleigh number (height based), $a = -4.17 \times 10^{-8}$ and $b = 1.4376$.

Shatikian et al. [30] reported that thick fins remained at the temperature of heated surface uniformly along the length. On the other hand, for the same length, thin fins experienced temperature gradient. From heat transfer point of view, it would be desirable if the fins perform at steady state. But too thick fins would lead to reduction in the number of fins. Therefore, the thickness of fins should also be optimized along with number of fins for the best performance of the system.

In LHTS units employed for solar heating systems, A/C systems, waste heat recovery systems, space based solar power systems, etc., the HTF exchanges heat with PCM stored in the unit. The performance of different types of heat exchangers used as LHTS units has been investigated by many researchers. For the recent review on various kinds of heat exchangers proposed by researchers, the readers are referred to [32]. Among these shell and tube/concentric double pipe heat exchangers have been proved as high efficient for minimum volume [33]. Few studies have assessed the performance enhancement due to employment of fins in shell and tube/concentric double pipe heat exchangers.

Lacroix [33] developed a three-dimensional numerical model for melting process in shell and tube LHTS with the PCM on the shell side and the HTF flowing inside. Annular fins were provided around the tube as shown in Fig. 5. Natural convection was included through effective thermal conductivity as a function of Rayleigh number in the conduction equation. The results showed that large amount of heat was conducted through the fins along the radial direction. For all ranges of mass flow rate and inlet temperature of HTF, considerable amount of increase in energy stored was observed due to the presence of fins. Increasing the

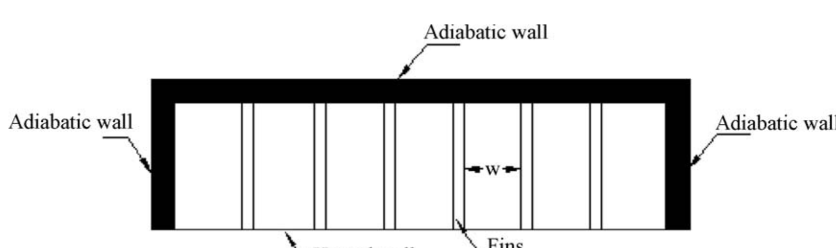


Fig. 4. Rectangular LHTS unit with vertical fins emerging from top heated wall [18].

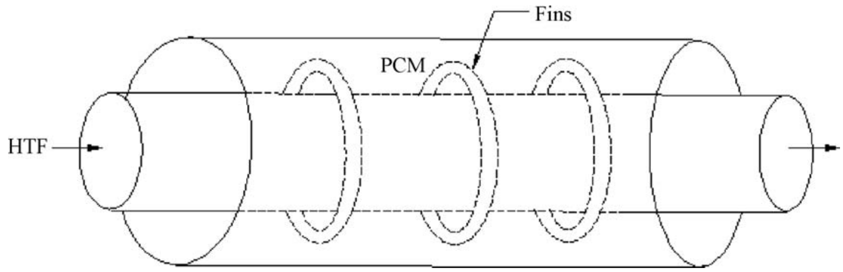


Fig. 5. Shell and tube LHTS unit with annular fins [33].

number of fins resulted in more increase in heat transfer rate and thus energy stored at all conditions. But the enhancement factor due to fins was dependent on mass flow rate and inlet temperature of HTF. It is from the fact that maximum enhancement was observed for moderate flow rates and small inlet temperature. On the other hand, for a larger mass flow rate and inlet temperature of HTF, the enhancement factor was not very significant even with more number of fins. Later, similar configuration was studied by Zhang and Faghri [34]. The numerical study included the effect of fin height. It has been shown that the liquid fraction of the PCM at any time during the melting could be increased by increasing the fin height. This is because, the melting fronts on both the sides of the fins were greatly affected by the height of the fin although the effect of fins on melt front was hardly felt in between the fins. The investigation also focused on the effect of initial subcooling on the position of melt front and liquid fraction. Generally many inorganic PCMs show considerable amount of subcooling, which in turn badly affects the system performance [35]. Zhang and Faghri [34] too observed significant reduction in performance due to subcooling. The effect of subcooling on performance was almost zero on both sides of the fins. This clearly shows that the fins are very effective in countering the reduction in performance due to subcooling effect of PCM.

Seeniraj et al. [36] investigated transient behavior of high temperature PCMs stored in finned shell and tube heat exchanger. Such high temperature LHTS units can be used in space based solar power plants. Since in solar space power systems microgravity conditions prevail, natural convection was assumed to be negligible. The study has revealed that if unfinned tube is used, then some quantity of PCM nearer to the exit of the tube would remain in solid state. This is because, nearer to the exit, the difference between HTF temperature and PCM's melting point would be very small. A few number of annular fins are capable of maintaining relatively high temperature difference between HTF and melting point and thus melting could be found everywhere in the axial direction. For a fixed size of LHTS unit, significant increase in energy stored was observed due to the presence of fins. However, the increase was substantial only in the initial stages of melting. A decrease in percentage increase in energy stored was observed as the process continued. At any particular time, the percentage increase in energy stored was directly proportional to number of fins. But adding more number of fins would effectively affect the amount of PCM stored. Hence, it is concluded that the number of fins is to be suitably selected to meet the desired amount of energy to be stored.

As reported by Seeniraj et al. [36], the enhancement factor due to fins decreases as the melting process continues. This is true only in case of conduction dominated melting. As mentioned earlier except in few cases, melting process is dominated by natural convection and in those cases, the enhancement factor due to fins would continuously increase throughout the melting process. This has been shown by Liu et al. [37]. They designed a new spiral twisted fins attached to the inner tube surrounded by a PCM stored outer tube. The inner tube was an electrical heating rod for supplying the heat to the PCM. During the pre-melting period which is conduction controlled, the temperature distributions in the PCM were more uniform than those without fins. This indicates faster heat transfer in case of finned system. Although the equivalent thermal conductivity was increased by fins during pre-melting period, the increase in equivalent thermal conductivity started decreasing after some time. But once melting begun, the equivalent thermal conductivity started increasing once again. This proves that fins are very effective not only in increasing the melting rate, but also in reducing the pre-melting time. It is also shown that better enhancement is possible if fins of small width are used. Fine fins of same amount of material provide more effective area than that of large fins and thus better conduction rate. Moreover, fine fins divide the annular space into more number of smaller sections, which enhances the natural convection.

The foregoing discussions have focused on adding fins to the PCM side. If HTF of low thermal conductivity (e.g. air) is used, then the main thermal resistance is experienced in the HTF side rather than in the PCM side [38]. Therefore, Zhang and Faghri [38] concentrated on enhancing the forced convective heat transfer inside the tube by employing internal longitudinal fins. As compared to unfinned system, in the finned system the melting process was accelerated because of increased forced convective heat transfer coefficient and direct heat transfer from fins to PCM. It should be noted that the fins were more efficient only at low Reynolds number. The effect of dimensions and number of fins on the liquid fraction was also investigated. Though it was observed that increase in thickness, height and number of fins led to increase in liquid fraction at any time, beyond some point the increase was less significant. Therefore, it is concluded that more number of fins would be beneficial if thicker and longer fins are used. It is also reported that the adverse effect of initial subcooling of PCM can be countered by using internal longitudinal fins.

2.2. Solidification

Contrary to melting process, solidification is dominated by conduction. During solidification natural convection exists only in the beginning and as the time goes the effect of natural convection becomes almost zero as compared to the effect of conduction [39]. The heat transfer characteristics of PCM during solidification have been explained by many investigators.

Stritih [8] compared the analytical results [conduction based] of solidification process in a rectangular storage unit with experimental results and obtained a good agreement between two. The natural convection was found to be 10 times lower than that in case of melting process. Ettouney et al. [19] studied the solidification in a shell and tube heat exchanger. It is reported that the solidification isotherms were almost parallel to the heat transfer surface and solidified layers took the same shape of the heat transfer surface. Hence, natural convection effects were found

to be negligible whether the direction of HTF flow was upward or downward. Ettouney et al. [17] obtained similar results even in spherical storage device. For the same module size, HTF temperature and HTF velocity, the heat transfer coefficient during melting was higher than that of during solidification. It indicates that melting was governed by natural convection where as it is not so in case of solidification.

These studies prove that in all configurations of LHTS, during solidification the solidified layers are formed from heat transfer surface and remain parallel to it. Although natural convection exists in the liquid PCM at earlier stages, it diminishes rapidly as the solidification progresses and the process becomes conduction dominated. This is because as the time goes, the liquid volume becomes smaller and smaller. Therefore, if fins are to be employed to enhance the solidification rate, then the sole purpose is to improve upon the conduction heat transfer.

To compare the heat transfer with and without fins in rectangular module, Stritih [8] estimated fin effectiveness experimentally. The effectiveness is defined as the ratio between heat flux with and that without fins. The results showed that the fin effectiveness was significantly high and because of that 40% reduction in solidification time was observed. Effect of vertical fins attached to horizontal constant temperature wall on solidification of high temperature PCM has been simulated by Guo and Zhang [40]. When the fins were not attached, solidification started on the wall and continuously moved away only in the vertical upward direction. However, after employment of vertical fins, the movement of solidified front was observed in vertical as well as in the horizontal direction simultaneously. More importantly, the rate of movement parallel to the fins was faster than that in the upward direction. The results also indicated that the discharge time with fins was almost 1/30th of that without fins. The time required for complete solidification was found to be decreasing almost linearly with number of fins. Similarly, increasing the fin thickness led to decrease in solidification time. There was also a critical value for fin thickness beyond which the effect on solidification was less significant.

Shatikian et al. [41] too observed that the solidification was not only initiated at the horizontal wall but also at the vertical fins attached to the wall. It is also added that at any time heat transfer from the fin to the wall was much higher than that coming directly from the PCM to the wall. Moreover, as the time elapsed, direct heat transfer from PCM to wall became negligible. This shows that fins increase the heat transfer rate from PCM and if fins are not provided, solidification may be terminated after some time. As in the case of system with vertical fins, the solidification rate can be effectively increased by increasing the number of horizontal fins attached to the vertical wall [26]. However, the numerical study by Gharebaghi and Sezai [25] has revealed that heat flux is higher for system with horizontal fins than that of system with vertical fins for any number of fins.

The study on performance enhancement due to fins during solidification has also been extended to cylindrical geometrics like shell and tube or double pipe arrangement. These studies have focused on both radial as well as axial fins attached to the heat transfer surface. Choi and Kim [42] conducted experimental study to determine the heat transfer characteristics of PCM during solidification in cylindrical storage system with radial fins. The results of temperature distributions showed that the temperature gradient at all radial positions were larger in case of finned system as compared to unfinned system. Thus, it is evident that there was an improved heat transfer between PCM and the tube due to radial fins. Also better axial conduction in the solid phase due to fins was observed, as the temperature distribution in the axial direction was more uniform in the finned system than those in unfinned system. Hence, the heat recovery was much faster due to radial fins. However, the effectiveness of the fins was found to be dependent on mass flow rate of HTF. For lower HTF mass flow rate, solidified layers were formed only on the small part of fins adjacent to the tube wall at earlier stages, though it was improved as the process progressed. At higher mass flow rates, solidified layers can be found on larger parts of fins right through the process and the best use of fins can be made. The effect of radial fins on enhancement has also been examined by Liu et al. [43]. They designed spiral twisted fins attached to the tube carrying HTF. It is reported that during solidification fins not only increase the conduction heat transfer, but also natural convection, which prevails at earlier stages. Because of this, employing fins were found to be more effective at earlier stages than at latter stages. Nevertheless, the enhancement factor was as high as 250% due to fins. It is also recommended to use less width fins as they produce more effective enhancement.

When shell and tube or concentric double pipe heat exchanger is used in LHTS units, usually PCM is stored in shell/annulus and the inner tube surface acts as heat transfer surface. During solidification, the solidified PCM between the tube and liquid PCM increases the thermal resistance and thus poor heat transfer to the liquid PCM, which is away from the tube. If fins are attached to the tube, the liquid PCM can have a better thermal contact with the heat transfer surface, which in turn reduces the thermal resistance. The above-mentioned studies have proved this point. However, Velraj et al. [44] have pointed out that further enhancement is possible if PCM is stored in the inner tube provided with longitudinal fins. Fig. 6 shows the LHTS unit with internal longitudinal fins. This is because, in this configuration, the thermal resistance experienced by the liquid PCM is uniformly reduced as the liquid PCM farthest away from the heat transfer surface can have maximum thermal contact with the fins. The authors have also observed additional heat flow which was in circumferential direction. Hence due to employment of longitudinal fins, higher surface heat flux was observed. Moreover, the surface heat flux could be increased to a larger extent with more number of fins. Although with fins the complete solidification time was approximately $1/n$ of that without fins, the effect of increasing the number of fins was more pronounced for larger tube radius. Recently, Castell et al. [45] have proved that adding vertical fins to the HTF side also enhances the performance of LHTS during solidification. This is because vertical fins on the HTF side significantly promote the natural convection within the HTF. The study focused on calculation of heat transfer coefficient through which it was found that the solidification time in the finned system was considerably less as compared to unfinned system. Therefore, it is concluded that in finned system same heat transfer coefficient of unfinned system can be achieved with less temperature difference. When the longer fins were used, there was decrease in heat transfer coefficient due to dampening effect on natural convection. Nevertheless, the solidification time was still less because of increase in heat transfer area. The LHTS unit with external longitudinal fins is shown in Fig. 7.

As mentioned earlier, the number/dimensions of the fins play very important role in promoting the natural convection during the phase change process. This is very crucial in convection dominated phase change process. Even in conduction dominated process the role of number/dimensions of the fins cannot be ruled out as they affect the amount of material stored in the unit of fixed size. In this case, choice of number of fins can be a compromise between the enhancement factor and amount of energy to be stored. Although different configurations of LHTS with various fin geometries have been studied widely, all works have not taken into account the effect of number/dimensions of the fins. This can be seen from Table 2, which presents the list of works carried out on finned LHTS units.

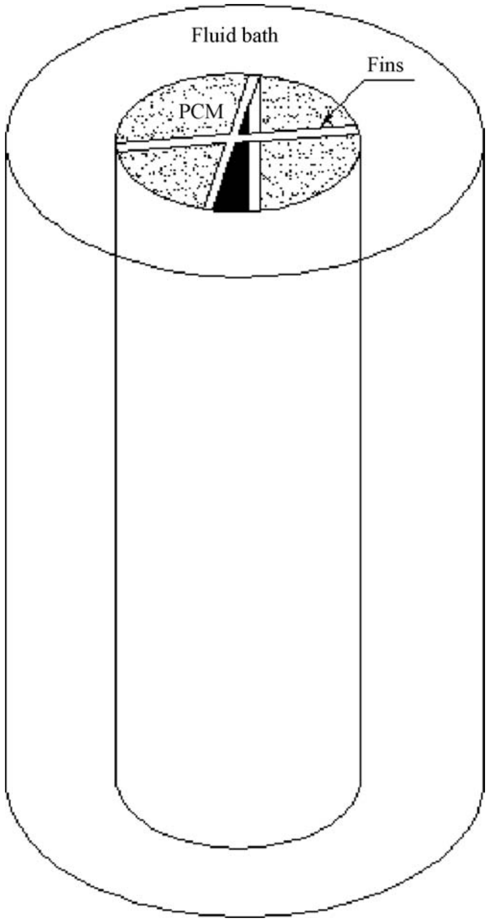


Fig. 6. LHTS unit with internal longitudinal fins [44].

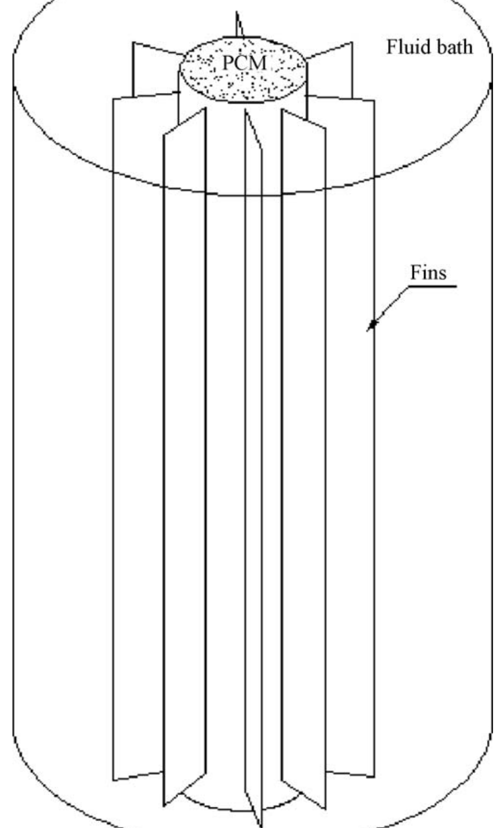


Fig. 7. LHTS unit with external longitudinal fins [45].

3. Employing multiple PCMs method

Employing multiple families of PCMs in LHTS system has been reported as another attractive performance enhancement technique in the literature. Employing multiple PCMs means, the LHTS system is packed with more than one PCM of different melting temperatures. The heat transfer rate in LHTS unit and thus the performance of the system during charging (melting) and discharging (solidification) mainly depends on the difference between the HTF temperature and the melting point of PCM. If single PCM is used in the unit, then this temperature difference would obviously decrease in the flow direction of HTF. This results in decrease in heat transfer rate and thus poor performance of the unit. If multiple PCMs of different melting temperatures are packed in the unit in the decreasing order of their melting points, then nearly a constant temperature difference can be maintained during melting process, even though the HTF temperature decreases in the flow direction. This leads to almost a constant heat flux to the PCM. During discharging, if the HTF flow direction is reversed then the PCMs remain in the increasing order of their melting points. Once again nearly constant heat flux but from the PCM to HTF is possible. The use of multiple PCMs in shell and tube is illustrated in Fig. 8.

The benefit of employing the multiple PCMs has been reported in new direction by Wang et al. [46]. The authors have introduced a new concept of homogeneous phase change process in which the phase change takes place everywhere in the PCM. This means the phase change rate of each component of PCM is same and remains constant during the process. Though a perfect homogenous PCM cannot be realized, it is suggested that if PCMs of different phase change temperatures are arranged in such a way that the phase change rate distribution is parabolic, then the phase change process would be homogeneous. It is also reported that with a nearly homogeneous phase change process, the phase change time can be reduced considerably. Hence, it can be stated that employing multiple PCMs seems to be a promising way to enhance the performance of the LHTS system during charging and discharging processes.

A good amount of work has been devoted to investigate the performance enhancement by employing multiple PCMs in different configurations of LHTS units. Farid and Kanzawa [47] employed three PCMs of different melting points packed in cylindrical capsules. Air was used as HTF. During both charging and discharging about 10% increase in heat transfer rate was obtained with three PCMs as the melting/solidification started in all three PCMs simultaneously, where as in single PCM system the phase change process started at different times. Experimental study by Michels and Pitz-Paal [48] has revealed the benefit of using multiple PCMs also in shell and tube module. The shell side was loaded with three PCMs and synthetic oil was allowed to flow through the inner tube. This unit corresponds to the one used for solar power plant. It was observed that in case of three PCMs unit larger potion of PCM underwent phase change process during the cycle. Hence, over a period of time three PCMs unit possessed higher phase change fraction and storage/discharge capacity as compared to the unit with single PCM of higher melting point.

In the above-mentioned configurations, HTF flows through the system and hence all the PCMs arranged in the flow direction (axial

Table 2
Studies on finned LHTS units.

Reference	System geometry	Geometry/orientation of fins	Phase change process	Effect of no. of fins	Effect of dimensions of fins
Lamberg and Siren [6]	Rectangular	Rectangular/between two vertical heated surfaces	Melting	Not included	Not included
Lamberg et al. [7]	Rectangular	Rectangular/between two vertical heated/cooled surfaces	Melting and solidification	Not included	Not included
Stritih [8]	Rectangular	Rectangular/vertical	Melting	Not included	Not included
Lacroix and Benmadda [18]	Rectangular	Rectangular/emerging from bottom heated surface	Melting	Included	Not included
Reddy [22]	Rectangular	Rectangular/emerging from top inclined heated surface	Melting	Included	Not included
Akhilesh et al. [24]	Rectangular	Rectangular/emerging from top heated surface	Melting	Not included	Not included
Gharebaghi and Sezai [25]	Rectangular	Rectangular/between two horizontal heated surfaces/ between two vertical heated surfaces	Melting and solidification	Included	Not included
Lacroix and Benmadda [26]	Rectangular	Rectangular/emerging from vertical heated surface	Melting and solidification	Included	Included (length)
Lamberg [27]	Rectangular	Rectangular/emerging from vertical heated surface	Melting	Included	Not included
Kandasamy et al. [29]	Rectangular	Rectangular/emerging from bottom heated surface	Melting	Not included	Not included
Shatikian et al. [30]	Rectangular	Rectangular, emerging from bottom heated surface	Melting	Included	Included (thickness)
Shatikian et al. [31]	Rectangular	Rectangular/emerging from bottom heated surface	Melting	Included	Included (length)
Lacroix [33]	Shell and tube	Annular/around HTF tube	Melting	Included	Not included
Zhang and Faghri [34]	Shell and tube	Annular/around HTF tube	Melting	Not included	Included (length)
Seeniraj et al. [36]	Shell and tube	Annular/around HTF tube	Melting	Included	Not included
Liu et al. [37]	Shell and tube	Spiral twisted/around HTF tube	Melting	Included	Included (width, thickness)
Zhang and Faghri [38]	Shell and tube	Rectangular/longitudinal, inside the HTF tube	Melting	Included	Included (length, thickness)
Lamberg [39]	Rectangular	Rectangular/between two vertical cooled surfaces	Solidification	Not included	Not included
Guo and Zhang [40]	Shell and tube	Annular/around HTF tube	Solidification	Included	Included (thickness)
Choi and Kim [42]	Shell and tube	Annular/around HTF tube	Solidification	Not included	Not included
Liu et al. [43]	Shell and tube	Spiral twisted/around HTF tube	Solidification	Not included	Included (width)
Velraj et al. [44]	Cylindrical tube	Rectangular/internal longitudinal	Solidification	Included	Not included
Castell et al. [45]	Cylindrical tube	Rectangular/external longitudinal	Solidification	Not included	Included (length)

direction) are in contact with the HTF. In solar thermal applications the LHTS system may be kept in the storage tank, which contains the HTF [49]. The PCM stored in the LHTS unit absorbs excess heat energy from the HTF during charging process and releases to HTF during discharging. In this case since the LHTS is surrounded by the HTF, there is no axial temperature variation within the HTF. In such kind of configurations, multiple PCMs should be arranged rather in radial direction than in axial direction in order to extract maximum benefit. As the centrally located PCM material in the single PCM unit has minimum thermal contact with the HTF, melting cannot be expected immediately. With multiple PCMs arrangement, it is possible to have lowest melting point PCM at the centre and other PCMs arranged in the increasing order of their melting points from the centre of the unit to the outer wall. This may lead to more or less simultaneous melting at all points as a nearly constant temperature difference can be maintained in the radial direction. One such arrangement has been investigated by Wang et al. [50]. They used three coaxial cylindrical tubes to store three PCMs and the entire unit was kept in water bath as shown in Fig. 9. The PCMs are arranged as explained above. The experiments were conducted only for charging process with different HTF temperatures. The results indicated that the melting time in three PCMs system was decreased by 37–42% as compared to that in single PCM module. This was due to the fact that the three PCMs unit terminated the melting process early by 15–25%.

The concept of multiple PCMs has also been extended to the LHTS systems in which there is no HTF. As mentioned earlier, these systems correspond to those used for electronic cooling. In this case, PCMs can be arranged in decreasing order of their melting points from the heated wall for charging and vice versa for discharging. A study on one such system has been undertaken by Wang et al. [51]. It is reported that if single PCM is used in the system then the phase change temperature distribution would be constant. On the other hand, with multiple PCMs linear phase change temperature distributions are possible. In the systems with constant temperature boundary conditions, a proper arrangement of different PCMs could lead to an optimum linear phase change temperature distributions. This results in 25% reduction in phase change time as compared to that in case of single PCM unit. It was also found that enhancement due to multiple PCMs was dependent on number of PCMs. The authors have concluded that practical and economical number of PCMs may vary from 5 to 10.

Multiple PCMs technique has found its application in the heat receivers of solar dynamic power system [52,53]. The PCM in the

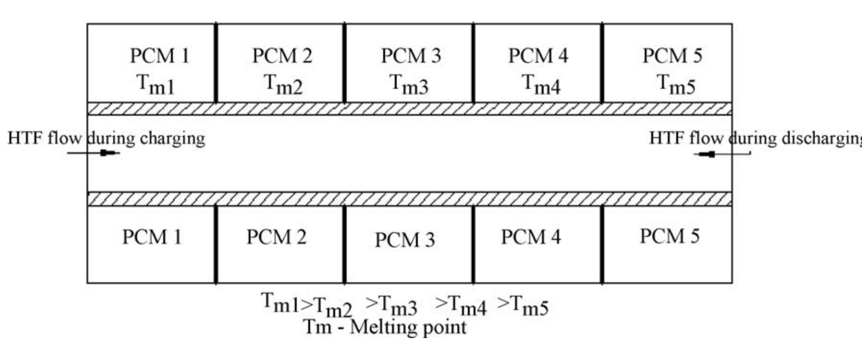


Fig. 8. Multiple PCMs in shell and tube LHTS unit.

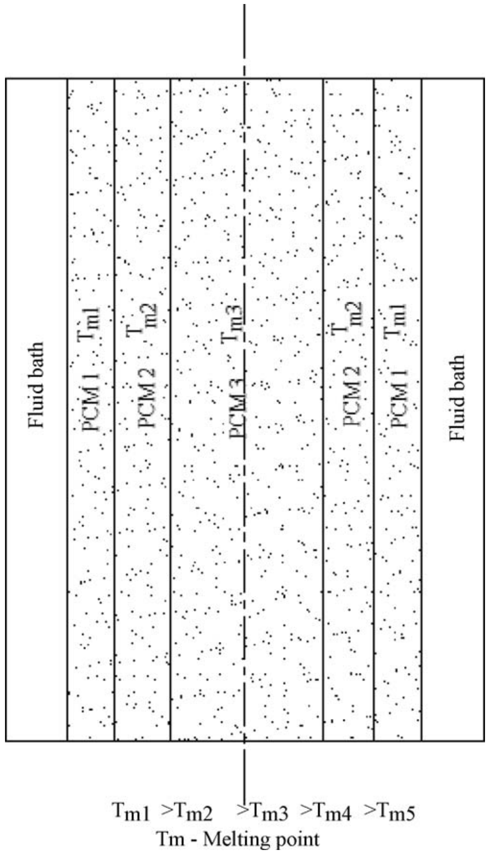


Fig. 9. Multiple PCMs in LHTS unit of coaxial cylindrical tubes [50].

heat receiver absorbs solar thermal energy during sunlight period and the absorbed energy is extracted by HTF during eclipse period. Like in other applications, the single PCM unit has been found to be inefficient and does not work properly [53]. Cui et al. [53] carried out numerical study on the solar dynamic power heat receiver with three PCMs. At the end of the charging period, three PCM module has a maximum of 0.74 liquid fraction as against 0.68 observed in single PCM module. Similarly, at the end of discharging process the liquid fractions of three PCMs and single PCM units were found to be 0.08 and 0.02 respectively. This shows a significant enhancement in performance with three PCMs. Hence, it is concluded that to transfer the same amount of heat energy, the weight of the heat receiver can be reduced considerably by employing multiple PCMs which is very important in space. It is also stated that reducing the maximum temperature of the tube walls is very crucial as it reduces the thermal stress and improves the reliability of the tube. Besides, there must be minimum fluctuation in the HTF exit temperature in order to improve the cycle efficiency. With three PCMs module reduced tube maximum temperature and less fluctuation in the HTF temperature could be achieved. Seeniraj and Narasimhan [54] also observed a nearly uniform temperature at the HTF outlet for a longer period in the five PCM shell and tube arrangement. Farid and Kanzawa [47] have shown that though at the beginning of the phase change processes the variation of HTF exit temperature in the multiple PCMs unit was similar to that of single PCM unit, there was sharp decrease in the rate of variation in case of multiple PCMs unit. However, towards the end of both the phase change processes multiple PCMs unit provided larger variation in the HTF exit temperature as compared to single PCM unit. Gong and Mujumdar [52] have pointed out the role of HTF mass flow rate in the variation of HTF exit temperature. It was found that at lower and higher HTF mass flow rates, the fluctuations in the HTF exit temperature were larger in case of system with multiple PCMs as compared to the one with single PCM. This has led to the conclusion that for a fixed size of the unit, there must be an optimum flow rate to keep the HTF exit temperature fluctuation minimal.

Although it is clear that multiple PCMs technique enhances the performance of LHTS systems, the enhancement factor is determined by the HTF inlet temperature and HTF mass flow rate [55]. The numerical study on the two PCMs shell and tube module by Adine and El-Qarnia [55] has revealed this fact. To compare the thermal performances of the two PCM and single PCM models during charging process, the term thermal storage efficiency was introduced. The thermal storage efficiency is defined as the ratio between the actual energy stored and maximum energy stored. With two PCMs system, a maximum storage efficiency of 0.98 was achieved for all HTF inlet temperatures and mass flow rates. From enhancement factor point of view, highest storage efficiency was obtained for lowest mass flow rate. When the mass flow rate was increased, the two PCMs system was efficient only for lowest HTF inlet temperature. Therefore, multiple PCMs unit is more efficient for low values of mass flow rate and inlet temperatures of HTF. Similarly the HTF inlet temperature plays important role even during charging. If very high difference between PCM melting point and HTF inlet temperature is maintained the performance would not be significant as higher temperature difference leads to excessive subcooling of PCM [52].

When multiple PCMs are employed to enhance the performance of LHTS systems, it is important to choose right combination of PCMs. This corresponds to appropriate difference between melting points of PCMs and relative proportions of the PCMs. Fang and Chen [56] conducted numerical study on shell and tube module during charging to examine the effect of different combinations of PCMs. Although this study is limited to three PCMs model, same conclusions may be extended to five or more number of PCMs models. Different sets of three PCMs were selected and in each case the difference between the melting temperatures of two adjacent PCMs was kept same. This difference between the melting temperatures was different for different cases. In all cases the middle PCM was same, named as benchmark PCM and chosen for single PCM unit. The results indicated that higher melt fractions and thus higher heat storage amounts were achieved for larger melting point differences with same benchmark PCM proportion. Increase in melt fraction/energy storage was observed in all cases when the benchmark PCM proportion was decreased. This is because decrease in benchmark PCM proportion led to increase in proportion of PCM with lowest melting point which needed less time to melt. However, in all cases there was an optimum value for benchmark PCM proportion to achieve the greatest melt fraction/energy storage. The results further showed that the optimum benchmark PCM proportion increased with increase in melting point difference between the PCMs. Watanabe and Kanzawa [57] studied the effect of melting point difference between the PCMs on both charging and discharging rates. Unlike in the work by Fang and Chen [56], Watanabe and Kanzawa [57] considered the difference between the highest and lowest melting points of PCMs in the set of PCMs. By increasing the melting point difference, both melting and solidification times could be reduced. However, beyond a value which is stated as optimum both the times started increasing. It is also shown that this optimum melting point difference increased with increase in difference between HTF inlet temperature and initial temperature of the PCMs. They have also presented simple expressions to roughly calculate the optimum melting point difference in terms of number of transfer units (NTU). Therefore, it can be concluded that while employing the multiple PCMs method, selection of appropriate

Table 3
Studies on multiple PCMs technique.

Reference	System geometry	Phase of operation	Nature of work	HTF	No. of PCMs	PCMs combination
Farid and Kanzawa [47]	Cylindrical tube loaded with PCM capsules	Charging and discharging	Numerical	Air	3	All arbitrary
Michels and Pitz-Paal [48]	Shell and tube	Charging only	Experimental and numerical	Oil	3	KNO_3, KNO_3 + KCl and $NaNO_3$ (all real)
Wang et al. [50]	Co-axial tubes	Charging only	Experimental	Water	3	Stearic acid, Sliced paraffin and lauric acid (all real)
Gong and Mujumdar [52]	Double pipe	Charging and discharging	Numerical	He/Xe	5	LiF + CaF_2 (real) and all others arbitrary
Cui et al. [53]	Double pipe	Charging and discharging	Numerical	He/Xe	3	LiF + CaF_2 (real) and all others arbitrary
Seeniraj and Narasimhan [54]	Shell and tube	Charging only	Numerical	Liquid Na	5	LiF + CaF_2, LiF + MgF_2 (both real) and all others arbitrary
Adine and El-Qarnia [55]	Shell and tube	Charging only	Numerical	Water	2	P-116 and n-octadecane (both real)
Fang and Chen [56]	Shell and tube	Charging only	Numerical	Air	3	All arbitrary
Watanabe and Kanzawa [57]	Cylindrical tube loaded with PCM capsules	Charging and discharging	Numerical	Water	15/30	All arbitrary
Domanski and Fellah [59]	Cylindrical tube	Charging and discharging	Numerical	Air	2	Both arbitrary

combination of PCMs is crucial to produce greatest performance enhancement.

The above-mentioned investigations indicate the thermal behavior of LHTS systems with multiple PCMs under different operating conditions. The information provided can be very useful for design optimization of such LHTS systems. Recently, Verma et al. [58] have pointed out that thermal analysis of LHTS systems based on only first law of thermodynamics may not produce a system with highest possible thermodynamic efficiency although workable designs may be possible. The authors thus have stressed the importance of exergy analysis based on second law of thermodynamics. Exergy analysis has also been carried out on LHTS systems with multiple PCMs.

Watanabe and Kanzawa [57] have presented guidelines to obtain maximum exergy efficiency from multiple PCMs systems. The results were obtained in terms of destroyed exergy and exergy efficiency at different operating conditions for both charging and discharging processes. For all values of HTF inlet temperature and initial temperature, there were optimum values of melting point difference between highest and lowest melting points. These optimum values led to lowest destroyed exergy and exergy efficiency. Further lowest destroyed exergy and thus highest exergy efficiency could be obtained only with smaller difference between the HTF inlet temperature and initial temperature of the PCMs. This is because the increase in the difference between the HTF inlet temperature and initial temperature of the PCMs would lead to increase in exergy loss to surroundings as the phase change process progresses. Domanski and Fellah [59] have compared the exergy efficiency of multiple PCMs unit with that of single PCM unit. The numerical results showed that the exergy efficiency of former was about 1.5 times that of latter. They have also proposed the melting point of the last PCM which is near the exit of the HTF should be close to ambient temperature so that minimum exergy loss to surroundings.

Although employing multiple PCMs, seems to be an attractive technique to enhance the thermal performance of conventional LHTS units, using multiple PCMs of different melting temperature along with finned surfaces would be better enhancement technique as the fins provide the compartments to store different PCMs [36]. Most of studies on employing multiple PCMs have been carried out only with arbitrary chosen materials, i.e. the melting points of the PCMs in the combination are based on arbitrary choice. This shows that studies still remain on a large scale to investigate the performance enhancement of LHTS with real-time PCMs of different combinations. Table 3 summarizes the various works on multiple PCMs technique with the important information of whether arbitrary chosen or real PCMs are considered.

4. Thermal conductivity enhancement

Although conventional PCMs offer high energy density, slower rates of melting and solidification limit the potential applications of LHTS systems in practical systems. This is due to the fact that all the conventional PCMs—both organic and inorganic possess very low thermal conductivity ranging from 0.1 to 0.6 W/m K. Table 4 lists thermal conductivity values along with latent heat values for few PCMs, which are identified as widely investigated by researchers so far. For comprehensive list, readers are referred to the review articles by Farid et al. [1], Sharma and Sagara [2] and Zalba et al. [3].

The thermal conductivity of conventional PCMs can be enhanced by employing high conductivity materials. The use of high conductivity materials to enhance the thermal conductivity of conventional PCMs has been dealt with in different ways by researchers, which can be summarized as follows:

Table 4
Thermal conductivity and latent heat of selected PCMs [1–3,60].

Name of the PCM	Thermal conductivity (W/m K)	Latent heat of fusion (kJ/kg)
Organics		
n-Octadecane	0.35 (solid) and 0.149 (liquid)	245
n-Docosane	0.22	194.6
Paraffin wax	0.514 (solid) and 0.224 (liquid)	251
Caprylic acid	0.149	149
Capric acid	0.153	153
Inorganics		
KNO_3	0.5	266
$NaNO_3$	0.5	172
$MgCl_2{\cdot}6H_2O$	0.694 (solid) and 0.57 (liquid)	168.6
$CaCl_2{\cdot}6H_2O$	1.088 (solid) and 0.54 (liquid)	190.8
Inorganic eutectics		
58.7%$Mg(NO_3){\cdot}6H_2O$–41.3%$MgCl_2{\cdot}6H_2O$	0.678 (solid) and 0.51 (liquid)	132
66.6%Urea–33.4%NH_4Br	0.682 (solid) and 0.331 (liquid)	161

- Impregnation of high conductivity porous material with the PCM.
- Dispersion of high conductivity particles in the PCM.
- Placing of metal structures in the PCM.
- Use of high conductivity, low density materials.

4.1. Impregnation of porous material

Porous structure may be either metal matrices made of aluminium, copper, etc., or naturally available porous material such as graphite. As far as metal matrices are concerned, recently Fiedler et al. [61] have found that copper matrices give approximately 80% increase in effective thermal conductivity as compared to that of aluminium matrices. More increase in effective thermal conductivity was found to be possible by using diamond coated copper matrices.

The effect of impregnating high conductivity porous matrix of different thermal conductivities and different porosities with PCM on thermal performance of LHTS system was investigated by Mesalhy et al. [62]. The numerical study was carried out to examine the melting process in a horizontal cylindrical annulus. The results indicated that the performance enhancement was dependent on both porosity and thermal conductivity of the matrix. In pure PCM, the rate of melting was less at the bottom portion of the container as compared to that at top portion as the melting process was convection dominated. With high conductivity porous matrix, the melting rate at lower portion could be increased. The enhancement due to porous structure was found to be dependent on porosity of matrix. All though for all porosity values higher melting rates were observed, decrease in porosity resulted in decrease in enhancement. Since low porosity values lead to higher effective thermal conductivity, theoretically there should be increase in performance enhancement. However, low porosity matrix dampens the motion of liquid PCM and thus natural convection within the liquid PCM. The results of this numerical study have proved this point as conduction like temperature profiles and streamlines were observed with lower porosity values. Krishnan et al. [63] obtained similar results from the numerical study on melting process in a rectangular enclosure filled with metal foam impregnated with PCM. In case of composite PCM, due to the restricted convective flow, the melt volume fraction at steady state was lower than that of pure PCM case. Nevertheless, substantial decrease in response time of the system was observed. Hence, it can be concluded that the porous matrix should possess not only high thermal conductivity but also high porosity for highest possible performance enhancement.

Graphite is known for its high thermal conductivity, high electrical conductivity and high absorbability. The thermal conductivity of graphite varies from 24 to 470 W/m K [64]. According to Haillot et al. [65], the thermal conductivity of PCM (0.2–1 W/m K) can be intensified by a factor of 5–100 depending upon the density of graphite added into the PCM. Cabeza et al. [66] have found that using PCM-graphite compound is the best option in applications like thermally stratified storage tank. The cheapest form of graphite is natural graphite flakes, which are composed of dense staked graphite layers. However, it is found that expanded graphite (EG) can be a better choice as it is of better absorbability due to high porosity. Generally EG can be prepared from natural graphite through chemical oxidation in the presence of concentrated sulphuric/nitric acid/mixture of sulphuric and nitric acids and followed by drying up process in oven and finally by rapid heating in a furnace. When the EG is mixed with PCM, the melted PCM will be absorbed in the pores of the EG results in composite PCM. The thermal conductivity and thermal capacity of the composite PCM depend upon the relative proportion of graphite and PCM.

Sari and Karaipekli [67] investigated thermal conductivity enhancement and storage enhancement due to the addition of EG in a paraffin based LHTS system. The PCM/EG composites were prepared with different mass fractions of EG. Besides analyzing the performance enhancement, the experimental study also focused on preparation of form-stable composite. The form-stable composite is nothing but composite of PCM/EG with no liquid PCM leakage. The composite PCM with 10% EG mass fraction was found to be more form-stable one as the paraffin was properly held by the capillary and surface tension forces of porous EG. Also the density of 10% EG composite was less than that of pure paraffin resulted in lighter LHTS unit with same volume. The thermal conductivity values obtained for composites with different EG mass fraction showed that the thermal conductivity can be increased by increasing the mass fraction of EG. The increase in mass fraction resulted in decrease in latent heat value and thus decrease in storage capacity. The optimum mass fraction was taken as 10% as this form-stable composite PCM possessed about four times higher thermal conductivity than that of pure paraffin with small decrease in latent heat value. It should be mentioned that the melting temperature of form stable composite was found to be lesser by 1.4 °C. The melting timings of pure paraffin and composite PCMs were compared to examine the impact of improvement in the thermal conductivity. The results indicated significant reduction in melting time (about 32%) when form-stable composite PCM was used in the LHTS system. Contrary to the results of Sari and Karaipekli [67], Yin et al. [68] have reported that the thermal conductivity of EG/paraffin composite steadily increased only up to the EG mass fraction value of 6.25. Beyond this value thermal conductivity started decreasing. The presence of some lacunas and gases in the loose structure of composite PCM with high EG mass fraction has been cited as reason the reduction in thermal conductivity. This indicates that composite should be prepared with appropriate mass fraction of graphite in such way the lacunas and gases are not present in the pores. Nevertheless, with 6.25% EG mass fraction the composite was from-stable, which presented significant increase in heat transfer rate not only during charging but also during discharging. The effect was more pronounced during charging. The decreases in melting and solidification times were about 65.3% and 26.2% respectively as compared to those with pure paraffin.

Recently, Kim and Drzal [69] used exfoliated graphite nanoplatelets (XGnP) to form graphite/paraffin composite. The XGnP, which are of less than 10 nm thick, and 15 μm average diameter can be obtained by pulverizing the EG using an ultrasonic processor. The results showed strong relation between mass percentage of XGnP and thermal conductivity. The continuous increase in thermal conductivity was observed up to the highest studied mass fraction of 7%. Besides, with all XGnP mass fractions, the latent heat values very closely matched with those of pure paraffin. As mentioned earlier, increase in mass fraction of expanded graphite would result in decrease in latent heat of PCM. In case of XGnP composite, since the high surface area of XGnP presented good dispersion in the PCM, there was no decrease in the latent heat. Hence, it can be stated that XGnP is more effective than EG as it enhances thermal conductivity with out reducing the storage capacity of pure PCM.

The use of graphite to improve the thermal conductivity of PCM is not only limited to low melting point PCMs such as paraffin, but also proposed for high melting point PCMs such as salts or eutectic mixtures [60,70]. Generally composite PCMs are made by mixing the graphites with molten PCM. The same method was adopted by Pincemin et al. [70] to prepare eutectic salt/graphite composite. Because of high viscosity of salt and similarity in density between salt and graphite, the graphite particles could be well dispersed within the molten salts and resulted in an isotropic composite.

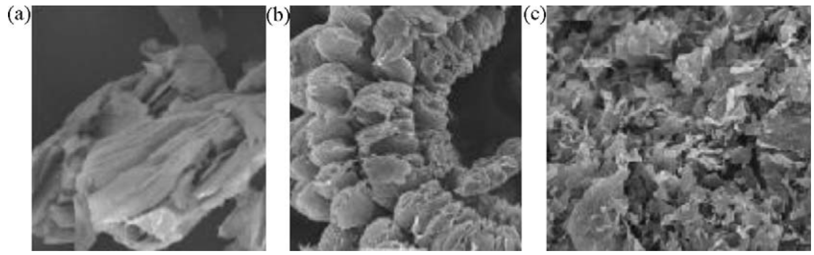


Fig. 10. Types of graphite.

However, this method was found to be less economical as PCM of high melting point needed more energy. Also corrosion effects on equipment and safety issues have been reported as limitations of this method. To overcome this problem, the authors adopted cold compression method for the preparation of composite. In cold compression method, after mixing the solid PCM with graphite powder physically, the mixture was compressed at room temperature. Due to the compression most of the porosity was removed resulted in a monolithic composite. This kind of composite can easily be shaped as per the geometry of the storage system. The composite obtained from cold compression method possessed anisotropic characteristics because of rearrangement of graphite layer orthogonally to the compression axis. The thermal conductivity measurement showed that radial thermal conductivity was much higher than that of axial one. For the same graphite quantity, the thermal conductivity of cold compressed composite was higher by two times as compared to that of composite obtained by mixing of graphite with molten PCM. Nevertheless, cold compressed composites were not found to be form-stable one as salt leakage was observed. This was due to the presence of impurities and mechanical stresses.

Pincemin et al. [60] used graphite powders of different particle sizes to prepare the composite with eutectic salt. The thermal conductivity was found to be dependent not only on graphite amount but also on particle size. From the results obtained, it is suggested that for higher graphite amount, larger particle size should be preferred as it presents better conductive network. On the other hand, for lower graphite quantity, particle should be of smaller size. As far as storage capacity is concerned, smallest particle size led to larger capacity when the graphite quantity was more. For smaller graphite content, the effect of particle size was not pronounced. The results also revealed that there was a decrease in phase change temperature variation due to the addition of graphite, i.e. the composite PCM possessed almost a congruent melting point. This is obviously an additional benefit as it would lead to more or less isothermal operation. The different types of graphites used by the researchers to make composite PCMs are shown in Fig. 10.

4.2. Dispersion of high conductivity particles in the PCM

Using graphite made composite PCMs has been proven as efficient and successful way in enhancing the performance of LHTS systems. However, graphite composites can be prepared only through various mechanical/chemical processes like heat treatment, drying, mixing, grinding/compression, etc., which are time and energy consuming processes. Moreover, Elgafy and Lafdi [71] have reported that the porosity of graphite is very crucial in deciding the effectiveness of the composites. If graphite of small mean pore size is used, then there may be decrease in latent heat value as small mean pore size hinders the molecular motion and thus very difficult to impregnate the porous media with the PCM. On the other hand, increasing pore size reduces the capillary force resulting in leakage of liquid PCM. Since the high conductivity metal particles are free from these shortcomings, dispersion of high conductivity particles into the PCM is relatively simpler technique to enhance the thermal conductivity of PCM.

Mettawee and Assassa [72] carried out experiments to investigate the enhancement in the performance of PCM based solar collector due to the dispersion of micro aluminium particles. During the charging process, the solar radiation was observed by the PCM stored in the container and during discharging, the cold water was supplied through the pipes embedded in the PCM. Although the heat transfer rate could be increased by increasing the mass fraction of aluminium, above 0.5 mass fraction, the increase in heat transfer rate was found to be insignificant. Due to increase in thermal conductivity, the charging time was decreased by 60% as compared to that of pure PCM. The effect was more pronounced during discharging, as the conduction dominated solidification presented more homogeneous process. To evaluate the overall benefit of embedding aluminium particles, the mean daily efficiency was calculated. The mean daily efficiency is defined as the ratio between heat gained by water during discharging and total incoming solar radiation during charging. The results showed significant increase in mean daily efficiency. For all mass flow rates of water, the highest mean daily efficiency obtained was 94% with composite PCM, where as with pure PCM it was only 55%. Although the performance enhancement due to particle addition is reported, the effect of adding the particles on the storage capacity has not been discussed in the paper. Khodadadi and Hosseinizadeh [73] have reported that the latent heat of PCM would decrease as the mass fraction of embedded particles is increased. They simulated the solidification of nanofluid [water + nano copper particles] in a square storage model. The speed of the solid/liquid interface during solidification was observed for pure PCM and for PCM with different particle mass fractions. At earlier stages there was not much increase in the speed of the interface due to the addition of particles. As the time elapsed the effect was more pronounced as the interface was at more advanced locations in case of higher mass fractions. This resulted in considerable reduction in overall solidification time. Besides copper and aluminium particles, silver has also been tried to obtain composite PCM. Zeng et al. [74] prepared a composite made of 1-tetradecanol and silver nanoparticles to investigate the effect of silver particles on the thermal performance of PCM. It is found that the thermal conductivity of the PCM increased as the loading of silver particles was increased. Besides this, silver particles brought in additional benefit as there was no strong reaction between silver and organic PCM. The thermal stability of the composite was almost same as that of pure PCM. However, the phase change temperature of the composite was found to be slightly lesser than that of pure PCM. Although it is reported that latent heat decreases with increase in mass fraction of particles [73,74], no attempt has been made in those studies to investigate the outcomes of different particles mass fraction. The effect of particle mass fraction has been extensively studied by Seeniraj et al. [75]. The numerical study was carried out on shell and tube arrangement. The increase in particle fraction reduces the volume occupied by the PCM. This leads to decrease in the amount

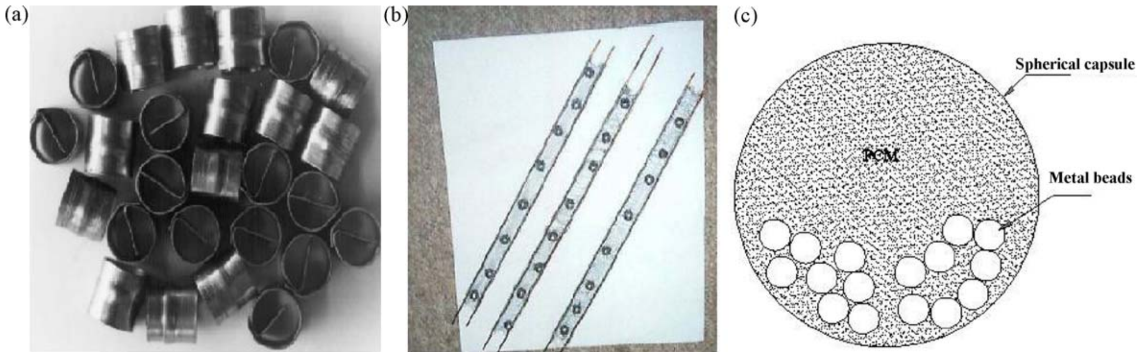


Fig. 11. Types metal structures: (a) lesser rings [49]; (b) metal balls combined with metal screens [76]; (c) metal beads [77].

of heat stored, even though higher heat transfer rate could be achieved. Therefore, it is important to determine the optimum particle fraction, so that maximum heat transfer rate with minimum loss in latent heat storage capacity can be achieved. For the determination of optimum particle mass fraction, Seeniraj et al. [75] calculated ratio of cumulative energy stored with particles and to that without particles. The results revealed the existence of optimum particle fraction at which highest ratio of cumulative energy stored was observed. As a matter of fact, at any given conditions there was a range of optimum particle fraction and it is suggested to choose lower value in the band to ensure high mass of PCM and thus more amount of energy stored. The analysis further indicated that the optimum mass fraction for maximum energy stored depended upon the particle thermal conductivity and maximum allowable radius for interface location. For higher values of particle thermal conductivity, the optimum mass fraction was also higher. Similarly, increase in optimum mass fraction was observed with increase in maximum allowable radius for interface. The maximum allowable radius for interface is determined by the dimensions of LHTS unit. Hence, an appropriate combination of particle thermal conductivity and particle mass fraction is quiet important when the conductivity particles are to be dispersed in the PCM to enhance the performance of the unit.

4.3. Placing of metal structures

Placing of metal structures into the PCM has also been addressed as one of the thermal conductivity enhancement techniques by few researchers. Velraj et al. [49] placed thin walled hollow cylindrical steel structures into paraffin stored in a cylindrical LHTS system. This structure is named as lesser rings (Fig. 11a). The results indicated considerable reduction in solidification time due to the addition of lesser rings. The time for complete solidification with lesser rings was approximately 1/9th of that without lesser rings, whereas with longitudinal fins, the time for complete solidification was around 1/4th of that without fins. One may come to a conclusion from this that lesser rings are more effective than fins. However, the above-mentioned reduction in solidification time could be achieved only with lesser rings occupying 20% of total volume as against fins occupying just 7% of total volume. This clearly shows that to get the same reduction in solidification time, more volume of lesser rings are required as compared to that of fins. It is also reported that the enhancement factor due to lesser rings depends upon the diameter of the cylindrical module, where as in case of fins, it remains almost constant for a fixed number of fins irrespective of diameter of the module. This proves that lesser rings are more effective than fins in larger storage systems.

This statement is not only valid for lesser rings, but also for other types of metal structures according to Ettouney et al. [76]. In a double pipe arrangement, stainless steel balls combined with stainless steel screens (Fig. 11b) were placed inside the PCM to increase the melting rate. The results revealed the fact that enhancement due to metal balls cum screens purely dependent on diameter and number of balls. Increasing diameter and number of balls resulted in increase in enhancement and the enhancement factor of up to 3 could be achieved. As mentioned earlier, in smaller systems the enhancement factor may be limited. This has also been proved by Ettouney et al. [77]. The study was carried out to investigate the effect of steel balls inserted into the PCM stored in small spherical module (Fig. 11c). Both melting and solidification processes were analyzed. The results showed only 15% reduction in melting and solidification times due to the addition of balls. This is obviously much smaller than that in larger systems.

4.4. Use of high conductivity and low density materials

Due to relatively high density, the metal particles/metal structures may settle on the bottom surface of the container and add considerable weight to the system. Besides, according to Fugai et al. [78], all metal particles are not compatible with all PCMs. For example, with paraffin, aluminium is compatible, where as copper and nickel are not compatible. Similarly, aluminium and copper are not compatible with some salt hydrates. Hence, there has been a search for low-density high conductivity additives, which should be compatible with all PCMs. Since the densities of carbon fibers are relatively lower than those of metals and the thermal conductivities are almost equal to that of aluminium and copper, these can be better alternatives to enhance the thermal performance of LHTS systems. Moreover, carbon fibers possess high corrosive resistance and hence compatible with most of the PCMs.

Elgafy and Lafdi [71] prepared a composite by adding carbon nanofibers of 100 nm average diameter and 20 μm average length, into paraffin wax using shear mixing and melting. The study focused on heat transfer characteristics during solidification. The thermal conductivity of the composite was found to be increasing almost linearly with increase in mass fraction of nanofiber. As a result, high solidification rate was observed. Even with 1% mass fraction of carbon fiber, the reduction in solidification time is reported as 23%. There was also no reduction in the storage capacity due to the additives as the output power increased linearly with increase in fiber mass fraction. The study was extended to investigate the effect of surface characteristics of fibers on solidification rate and found higher transfer rate with surface treated fibers than that with fibers of untreated surface. The study has also revealed the importance of uniform distribution of fibers in the PCM to obtain further enhancement in the performance.

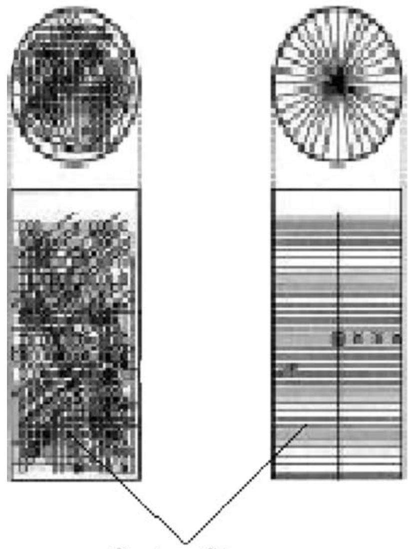


Fig. 12. Distribution of carbon fibers in cylindrical capsule [78]: (a) random distribution; (b) brush type.

The importance of uniform distribution of carbon fibers has also been reported by Fugai et al. [78]. In a cylindrical capsule, carbon fibers were added in the PCM in two ways. In the first case fibers were randomly distributed, where as in the second case brush type fibers were used. The two cases of distribution of carbon fibers in cylindrical capsule can be seen in Fig. 12. The effective thermal conductivity with brush type was found to be three times higher than that with random type. This is because in brush type the fibers were distributed uniformly in such a way all the fibers were arranged in radial direction, which was the heat flow direction. For lower mass fraction of fibers, the randomly distributed arrangement could not present higher melting rate than that with pure paraffin, even though the effective thermal conductivity of former is greater than that of latter. This is due to the loss in natural convection in case of randomly distributed arrangement. On the other hand, the loss in natural convection could not affect the higher melting rate in case of brush type. This shows that the fibers should be arranged in such a way that they are oriented in the direction of heat flow. The superiority of brush type arrangement also in shell tube arrangement is proved by Fugai et al. [79]. They could achieve 30% and 20% higher solidification rate and melting rate respectively with 1% mass fraction carbon brush type fibers as compared to those with pure PCM. Hamada et al. [80] compared the fiber brush with fiber chips. The experiments were conducted for melting process and results revealed that fiber chips resulted in higher thermal resistance near the heat transfer tube and thus the over all heat transfer rate was lower than that for fiber brush type. According to Fugai et al. [81], when carbon fiber brushes are used around heat transfer tube, then there was a critical diameter for the brush. The authors observed that the thermal response of the system increased with increase in brush diameter. When the diameter of the brush was increased beyond a value at which the brushes cross the heat transfer tubes, there was no further improvement in thermal response. This was due to the fact that beyond this critical diameter, the thermal resistance between fibers and the tube surface was higher. Hamada et al. [82] have also discussed the critical diameter of carbon fiber brushes. It is stated that if brush diameter is too large, then the fibers leaving the heat transfer surface form a region where the density of fibers is low. This low density region would prevent the further improvement in heat transfer rate. Hence, it is important to make sure that there is no low-density fiber region to get maximum benefit out of carbon fibers.

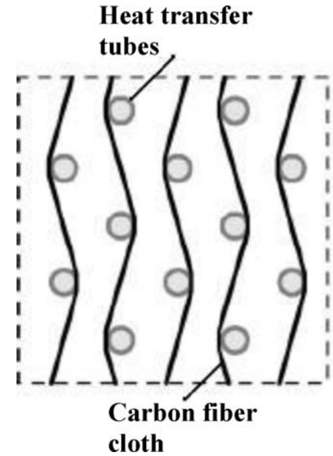


Fig. 13. Carbon fiber cloths stretched over heat transfer tube [84].

From economical point of view, one may think carbon fibers are expensive. However, Hamada and Fugai [83] have reported that carbon fiber brushes could effectively reduce the cost and space. The experiments were carried out on carbon fiber brushes inserted LHTS unit used for air conditioning system. The LHTS unit without carbon brushes needed relatively bigger size to produce the required thermal output than that of LHTS with 0.8 volume fraction of carbon fiber brushes. On the other hand, for the same thermal output the cost of latter was only 75% of that of former. As mentioned earlier, there exists thermal contact resistance between carbon fiber brush and heat transfer surface. This may affect the heat transfer enhancement especially when the volume fraction of fiber is less. Very recently, Nakaso et al. [84] have proposed a new technique of using carbon fibers. They used carbon fiber cloths in place of carbon fiber brushes. The cloths made of carbon fibers were highly stretched over the heat transfer surface from end to end of the tubes. The application of carbon fiber cloth is shown in Fig. 13. It is reported that these cloths with high surface density can act as fins. The results showed that fiber cloths of 0.42% volume fraction presented the same thermal performance of fiber brushes of 0.75% volume fraction. It is clear that low volume/mass fraction is desirable as reduction in storage capacity due to the additives would be negligible.

The review on thermal conductivity enhancement methods has revealed that the phase change rate (melting/solidification) can be increased considerably by adding high conductivity substances. In general, however, these additives may lead to loss of storage capacity of pure PCM. The loss in storage capacity limits the mass/volume fraction of additives. Therefore it should be mentioned that while employing such additives, it is important to estimate the optimum mass/volume fraction of additives. Table 5 presents the list of works carried out to investigate the thermal response of PCM under the influence of various high conductivity additives.

5. Microencapsulation of PCM

It is also proposed that the heat transfer rate between PCM and source/sink can be increased by using microencapsulated PCMs. As the name suggests microencapsulated PCMs are microsize PCM in liquid/solid (core) form enveloped within a solid structure (shell/wall). The shell can be made of wide range of materials including natural and synthetic polymers [85]. Microencapsulation of PCMs can be achieved by two methods namely chemical (e.g. coacervation, complex coacervation, interfacial methods) and mechanical or physical methods (e.g. spray drying method). For the complete

Table 5
Studies on PCM thermal conductivity enhancement by additives.

Reference	Type of additive	PCM	Phase change process	Investigation on mass/volume fraction of additive
Pincemin et al. [60]	Natural graphite, expanded graphite and ground expanded graphite	$NaNO_3 + KNO_3$	Both melting and solidification	Not investigated
Fiedler et al. [61]	Aluminium/copper metal matrix	Paraffin	Not investigated	Not investigated
Mesalhy et al. [62]	Metal matrix	Not available [non-dimensional study]	Melting only	Not investigated
Krishnan et al. [63]	Metal matrix	Not available [non-dimensional study]	Melting only	Not investigated
Haillot et al. [65]	Expanded graphite	Paraffin, stearic acid, sodium acetate hydrate and barium hydroxide octa hydrate	Both melting and solidification	Investigated
Cabeza et al. [66]	Graphite	Sodium acetate hydrate	Both melting and solidification	Not investigated
Sari and Karaipekli [67]	Expanded graphite	n-Docasane	Melting only	Investigated
Yin et al. [68]	Expanded graphite	Paraffin	Both melting and solidification	Investigated
Kim and Drzal [69]	Exfoliated graphite	Paraffin	Both melting and solidification	Investigated
Mettawee and Assassa [72]	Aluminium particles	Paraffin	Both melting and solidification	Investigated
Khodadadi and Hosseinizadeh [73]	Copper nano-particles	Water	Solidification only	Investigated
Zeng [74]	Silver nano-particles	1-Tetradecanol	Both melting and solidification	Investigated
Seeniraj et al. [75]	Metal particles	Not available [non-dimensional study]	Melting only	Not investigated
Velraj et al. [49]	Lesser rings	Paraffin	Solidification only	Not investigated
Ettouney et al. [76]	Metal screens and beads	Paraffin	Melting only	Not investigated
Ettouney et al. [77]	Metal beads	Paraffin	Both melting and solidification	Not investigated
Fugai et al. [78]	Carbon fibers	Paraffin	Not investigated	Not investigated
Fugai et al. [79]	Carbon fibers	Paraffin	Both melting and solidification	Not investigated
Hamada et al. [80]	Carbon fibers	n-Octadecane	Melting only	Investigated
Fugai et al. [81]	Carbon fibers	n-Octadecane	Melting only	Investigated
Hamada et al. [82]	Carbon fibers	n-Octadecane	Melting only	Not investigated
Hamada et al. [83]	Carbon fibers	Paraffin	Both melting and solidification	Investigated
Nakaso et al. [84]	Carbon fiber cloths	Paraffin	Solidification only	Not investigated

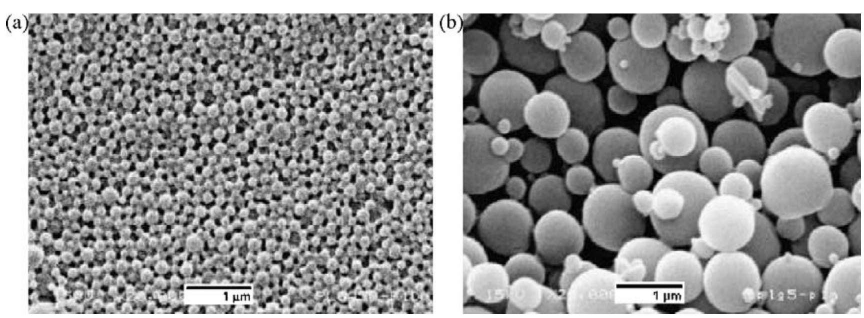


Fig. 14. Microscope profiles of microencapsulated PCMs [85]: (a) from spray drying method; (b) from coacervation method.

procedure of these methods readers are referred to [85–87]. The microscope profiles of microencapsulated PCMs obtained from spray drying and coacervation methods can be seen from Fig. 14. The thermal performance of microencapsulated PCMs can be expected to be better than that of conventional PCMs. This is because small PCM particles provide larger heat transfer area per unit volume and thus higher heat transfer rate. Besides this, microencapsulated PCMs bring in more advantages like less

Table 6
Studies on microencapsulation of PCM.

Reference	Core PCM	Shell material	Microencapsulation method	Comparative evaluation
Hawlader et al. [85]	Paraffin wax	Gelatin + acacia	Complex coacervation/spray drying	No
Chen et al. [86]	1-Bromohexadecane	Amnoplastics	Not available	No
Alkan et al. [87]	n-Docasane	Polymethylmethacrylate	Emulsion polymerization	No
Rao et al. [94]	n-Octadecane	Polymethylmethacrylate	Not available	No
Hawlader et al. [96]	Paraffin wax	Gelatin + acacia	Complex coacervation	No
Zou et al. [97]	Hexadecane	4-Diisocynate/ethylenediamine	Interfacial polycondensation	No
Choi et al. [98]	Tetradecane	Melamine–formaldehyde	In situ polymerization	No
Ozonur et al. [99]	Coco-fatty acid	Gelatin + gum arabic	Coacervation/complex coacervation	Yes (during both charging and discharging)
Hawlader et al. [100]	Paraffin wax	Gelatin + acacia	Coacervation	No

Table 7
Mathematical modeling of LHTS systems employing performance enhancement techniques.

Reference	System geometry	Enhancement technique	Phase change process	Numerical formulation	Performance parameters investigated
Lamberg et al. [7]	Rectangular	Fins	Melting and solidification	Enthalpy/effective heat capacity	Phase change rate
Lacroix and Benmadda [18]	Rectangular	Fins	Melting	Enthalpy	Melting rate and melt fraction
Reddy [22]	Rectangular	Fins	Melting and solidification	Enthalpy	Melt fraction and average HTF temperature
Gharebaghi and Sezai [25]	Rectangular	Fins	Melting and solidification	Enthalpy	Melt fraction and heat flux
Lacroix and Benmadda [26]	Rectangular	Fins	Melting and solidification	Enthalpy	Melting rate and melt fraction
Shatikian et al. [30]	Rectangular	Fins	Melting	Enthalpy	Melt fraction and heat flux
Shatikian et al. [31]	Rectangular	Fins	Melting	Enthalpy	Melt fraction
Lacroix [33]	Shell and tube	Fins	Melting	Enthalpy	Melt fraction, heat transfer rate and energy stored
Zhang and Faghri [34]	Shell and tube	Fins	Melting	Effective heat capacity	Melt fraction
Seeniraj et al. [36]	Shell and tube	Fins	Melting	Enthalpy	HTF exit temperature and energy stored
Zhang and Faghri [38]	Shell and tube	Fins	Melting	Effective heat capacity	Melt fraction
Lamberg [39]	Rectangular	Fins	Solidification	Effective heat capacity	Melt fraction and solidification rate
Guo and Zhang [40]	Shell and tube	Fins	Solidification	Enthalpy	Melt fraction, heat flux and time for complete solidification
Velraj et al. [44]	Cylindrical tube	Fins	Solidification	Enthalpy	Melt fraction, heat flux and time for complete solidification
Farid and Kanzawa [47]	Cylindrical tube loaded with PCM capsules	Multiple PCMs	Melting and solidification	Not available	HTF exit temperature and heat stored/discharged
Cui et al. [53]	Double pipe	Multiple PCMs	Melting and solidification	Enthalpy	Melt fraction and HTF exit temperature
Seeniraj and Narasimhan [54]	Shell and tube	Multiple PCMs	Melting	Enthalpy	Energy stored and HTF exit temperature
Adine and El-Qarnia [55]	Shell and tube	Multiple PCMs	Melting	Enthalpy	Melt fraction, energy stored and heat transfer rate
Watanabe and Kanzawa [57]	Cylindrical tube loaded with PCM capsules	Multiple PCMs	Melting and solidification	Second law based formulation	Exergy efficiency and exergy destroyed
Domanski and Fellah [59]	Cylindrical tube	Multiple PCMs	Melting and solidification	Second law based formulation	Exergy efficiency and exergy stored
Pincemin et al. [60]	Rectangular	Additive-graphite additive	Melting and solidification	Effective heat capacity	Phase change rate
Krishnan et al. [63]	Rectangular	Additive-metal matrix	Melting	Enthalpy	Melt fraction
Khodadadi and Hosseinizadeh [73]	Square	Additive-copper nano-particles	Solidification	Enthalpy	Melt fraction
Seeniraj et al. [75]	Shell and tube	Metal particles	Melting	Enthalpy	Energy stored and effectiveness
Fugai et al. [79]	Shell and tube	Additives-carbon fiber brushes	Melting and solidification	Effective heat capacity	HTF exit temperature
Hamada et al. [83]	Shell and tube	Additives-carbon fiber brushes	Melting and solidification	Effective heat capacity	Thermal output, energy stored/retrieved and heat transfer rate
Nakaso et al. [84]	Shell and tube	Additives-carbon fiber cloths	Solidification	Effective heat capacity	Heat release rate

reaction of PCM with container material, ability to withstand volume change during phase change, etc. [85].

The above stated advantages in general and easy incorporation in particular have made microencapsulated PCMs very attractive in improving the thermal performance of building materials [88–90], textile fabrics [91,92] and Thermal fluids [86,87,93–95].

Many studies have been carried out on microencapsulated PCMs with different combination of PCMs and shell materials like paraffin wax as core and gelatin + acacia as shell [85,96], 1-bromohexadecane as core and amnoplastics as shell [86], n-docasane as core and polymethylmethacrylate as shell [87], n-octadecane as core and polymethylmethacrylate as shell [95], hexadecane as core and 4-diisocynate + ethylenediamine as shell [97], tetradecane as core and melamine–formaldehyde as shell [98], coco fatty acid mixture as core and gelatin + gum Arabic as shell [99], etc.

These studies mainly focused on preparation and characterizations of microencapsulated PCMs. Alkan et al. [87] have showed that microcapsules containing n-docasane have good thermal and chemical stability. The results of accelerated thermal cycle testing showed no significant change in the phase change temperature and enthalpy even after 5000 thermal cycles. Hawlader et al. [100] prepared relatively larger capsules of paraffin (2.833 mm diameter) and found that the storage capacity of capsules remained almost same even after 1000 thermal cycles. The geometrical structure could be retained after 1000 thermal cycles. Zho et al. [97] have reported that microencapsulated hexadecane can be suffered up to a temperature of 282 °C. Similarly, as reported by Ozonur et al. [98], microencapsulated fatty acid mixture could retain the geometric profiles even after 50 cycles and the chemical structure of the pure PCM would remain same after the microencapsulation. Hence, it is clear that the commonly used PCMs can be successfully microencapsulated which are proven to be thermally and chemically stable. However, Hawlader et al. [96] have pointed out that the ratio between PCM and wall material is critical in determining the quantity of PCM that can be encapsulated out of original PCM quantity. It is found that increase in wall material led to encapsulation of more PCM. However, this would result in less quantity of PCM and hence decrease in storage capacity. The decrease in storage capacity due to encapsulation would be more when physical method (spray drying method) is used as compared to that with chemical method (complex coacervation) according to Hawlader et al. [85].

As mentioned earlier, due to large heat transfer area per unit volume of the container, microencapsulated PCMs can be expected to present higher transfer rate than that of pure PCMs. Higher transfer rate results in large energy storage and release capacity and thus Hawlader et al. [85] and Hawlader et al. [96] have recommended microencapsulated paraffin for applications like solar energy storage system. However, the results obtained by Ozonur et al. [99] showed that microencapsulated fatty acid presented higher heat transfer rate as compared to that of pure fatty acid only during charging. On the other hand, during discharging, pure PCM was found to be with higher heat transfer rate. Except the study by Ozonur et al. [99], none of the other works on microencapsulated PCMs has compared the performance of the microencapsulated PCM with that of pure PCM. In the work by Ozonur et al. [99], the PCM used was fatty acid mixture which has the melting point range of 22–24 °C. Hence, the pure fatty acid was in liquid state at room temperature and during charging, the energy was stored in the form of sensible heat. On the other hand, microencapsulated fatty acid was found to be with melting point range of 29–31 °C and hence phase change could be observed when heated from room temperature. Therefore, this comparative study has not addressed the effect of microencapsulation on the heat transfer enhancement during phase change process. Recently, Regin et al. [101] have reported that the rigidity of the microencapsulated PCM matrix dampers the natural convection and thus reduces the heat transfer rate. If a microencapsulated PCM should replace the relatively cheaper conventional PCM, then there must be a substantial heat transfer enhancement. As of now, it is not much clear, as none of the works has extensively compared the performance of microencapsulated PCM with that of pure PCM. The list of works on microencapsulated PCMs is given in Table 6. Hence, it can be stated that more work is needed especially on comparative study between pure PCMs and microencapsulated PCMs in order to assess the performance enhancement due to microencapsulation of commonly used PCMs.

6. Mathematical modeling of LHTS systems employing performance enhancement techniques

Phase change problems are examples of what are closely referred to as moving boundary problems and their study presents one of the most exciting and challenging areas of current applied mathematical research. The existence of a moving boundary generally means that the problem does not admit a simple closed form analytical solution and accordingly much research has focused on approximate solution techniques. In general, phase change problems involve a transient, non-linear phenomenon with a moving liquid–solid interface whose position is unknown a priori and also flow problems associated with HTF. In addition, the two phases of PCM may have different properties and configuration of the LHTS unit may differ with the applications. Substantial number of numerical based studies on LHTS units employing enhancement techniques and on their performance measurement is available in the literature. The numerical formulations widely implemented so far are enthalpy method and effective heat capacity method.

In the enthalpy method, the enthalpy which is a function of temperature is considered as a dependent variable along with temperature. Thus the enthalpy based conduction equation is valid for both solid and liquid phases. Besides, it is valid for solid–liquid interface. Therefore, there is no need to track the interface which makes this formulation attractive [102]. In the effective heat capacity method, the heat capacity of the PCM during phase change process (effective heat capacity) is introduced. The effective heat capacity is directly proportional to the stored/released energy during the phase change and the specific heat. Therefore, with effective heat capacity it is also possible to describe the non-isothermal phase change in the PCM. For the details of these two formulations, readers are referred to [103] for enthalpy method and [27] for effective heat capacity method. Besides these two formulations, Yingqiu et al. [104] have proposed another method called alternate thermal resistance method.

The numerical studies on LHTS units employing performance enhancement technique have mainly focused on evaluation of melting/solidification time, heat transfer rate and amount of energy stored/retrieved in comparison with those of system without enhancement techniques. As mentioned earlier, Verma et al. [58] have pointed out the importance of exergy analysis of LHTS units. In view of that, it can be mentioned that a numerical study based on exergy analysis would be a better option for the complete evaluation of enhancement in performance under the influence of possible enhancement techniques. To the best of the authors' knowledge very few numerical investigations based on exergy analysis are reported till date and this can be drawn as a gap in the contemporary research. Table 7 summarizes the various numerical investigations on LHTS systems employing performance enhancement techniques.

7. Conclusions

The techniques employed to enhance the performance of LHTS units have been reviewed. Various techniques reviewed in this paper include using extended surfaces, employing multiple PCM's method, thermal conductivity enhancement and micro-encapsulation of PCM. Considerable amount of work has been devoted to assess the effect of those techniques on thermal response of LHTS units. This review of those works aims at providing necessary information on features and limitations of each technique to enable further research in the area. Exergy analysis of LHTS units employing performance enhancement techniques may be taken as a main aspect in future mathematical modeling based research works.

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